

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
2 October 2003 (02.10.2003)

PCT

(10) International Publication Number
WO 03/080241 A1

(51) International Patent Classification⁷: **B01J 27/26, C08G 65/30**

(21) International Application Number: PCT/US03/07999

(22) International Filing Date: 17 March 2003 (17.03.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/366,758 21 March 2002 (21.03.2002) US

(71) Applicant (*for all designated States except US*): **DOW GLOBAL TECHNOLOGIES, INC.** [US/US]; Washington Street, 1790 Building, Midland, MI 48674 (US).

(72) Inventor; and

(75) Inventor/Applicant (*for US only*): **WEHMEYER, Richard, M.** [US/US]; 205 Zinnia, Lake Jackson, TX 77566 (US).

(74) Agent: **COHN, Gary, C.**; Gary C. Cohn PLLC, 4010 Lake Washington Boulevard NE, Suite 105, Kirkland, WA 98033 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD FOR PREPARING METAL CYANIDE CATALYST COMPLEXES USING PARTIALLY MISCIBLE COMPLEXING AGENTS

(57) Abstract: Double metal cyanide catalysts (DMC) are complexed with complexing agents that are miscible in poly(propylene



03/080241 A1

METHOD FOR PREPARING METAL CYANIDE CATALYST COMPLEXES USING PARTIALLY MISCIBLE COMPLEXING AGENTS

BACKGROUND OF THE INVENTION

5 This invention relates to methods for making metal cyanide catalysts complexes and to methods for polymerizing alkylene oxides in the presence of a metal cyanide catalyst.

 Polyethers are prepared in large commercial quantities through the polymerization of alkylene oxides such as propylene oxide and ethylene oxide.
10 This polymerization reaction is usually conducted in the presence of an initiator compound and a catalyst. The initiator compound usually determines the functionality (number of hydroxyl groups per molecule of the polymer) and in some instances imparts some desired functionality. The catalyst is used to provide an economical rate of polymerization.

15 Metal cyanide complexes are becoming increasingly important alkylene oxide polymerization catalysts. These complexes are often referred to as "double metal cyanide" or "DMC" catalysts, and are the subject of a number of patents, including, for example, U.S. Patent Nos. 3,278,457, 3,278,458, 3,278,459, 3,404,109, 3,427,256, 3,427,334, 3,427,335 and 5,470,813, among many others. In
20 some instances, these complexes provide the benefit of fast polymerization rates and narrow polydispersities. Additionally, these catalysts are associated with the production of polyethers having very low levels of monofunctional unsaturated compounds.

 It is often desirable to remove residual DMC catalyst from polyethers.
25 Various methods of accomplishing this have been developed, but the simplest method would be a simple filtration or phase separation. However, DMC catalysts that can be easily and effectively filtered from the polyol have not been commercially established.

 Thus, it would be desirable to provide metal cyanide catalyst complex that
30 exhibits good catalytic activity and can be simply and easily removed from a polyether polyol.

SUMMARY OF THE INVENTION

 This invention is a metal cyanide catalyst complexed with a complexing
35 agent that is miscible in a poly(propylene oxide) at an elevated temperature, but

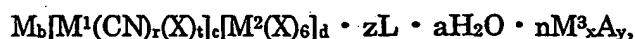
which is not miscible in the poly(propylene oxide) at a lower temperature at which the poly(propylene oxide) is a liquid.

In another aspect, this invention is a metal cyanide catalyst complexed with an immiscible complexing agent comprising a poly(ethylene oxide) polymer or
5 block copolymer having poly(ethylene oxide) blocks and blocks of another monomer or monomers, wherein the immiscible complexing agent is miscible in a poly(propylene oxide) at an elevated temperature, but which is not miscible in the poly(propylene oxide) at a lower temperature at which the poly(propylene oxide) is a liquid.

10 In another aspect, this invention is a process wherein a catalyst of any of the preceding aspects is mixed with an alkylene oxide and the resulting mixture subjected to conditions sufficient to polymerize the alkylene oxide to form a poly(alkylene oxide).

15 DETAILED DESCRIPTION OF THE INVENTION

The metal cyanide catalyst advantageously has the structure represented by the general structure:



wherein M and M³ are metal ions that form an insoluble precipitate with the
20 M¹(CN)₆ and M²(X)₆ ions,

M¹ and M² are transition metal ions;

X represents a group other than CN⁻ that coordinates with the M¹ ion;

r and t are numbers that represent the number of CN⁻ and X groups, respectively, that are coordinated with the M¹ ion (r + t preferably equals 6 and t is most
25 preferably zero);

L represents the complexing agent;

A represents an anion that forms a salt with the M³ ion;

b, c and d are numbers that reflect an electrostatically neutral complex, with the ratio of c:d being from about 50:50 to about 100:0;

30 x and y are numbers that reflect an electrostatically neutral salt of M³ and A;

z, a and n are positive numbers (which may be fractions) indicating the relative quantities of the complexing agent, water, and M³_xA_y, respectively, and

a is zero or a positive number indicating the relative quantity of water molecules.

M¹ is preferably Fe⁺³, Fe⁺², Co⁺³, Co⁺², Cr⁺², Cr⁺³, Mn⁺², Mn⁺³, Ir⁺³, Ni⁺²,
35 Rh⁺³, Ru⁺², V⁺⁴ and V⁺⁵. Among the foregoing, those in the plus-three oxidation

state are more preferred. Co^{+3} and Fe^{+3} are even more preferred and Co^{+3} is most preferred. M is preferably a metal ion selected from the group consisting of Zn^{+2} , Fe^{+2} , Co^{+2} , Ni^{+2} , Mo^{+4} , Mo^{+6} , Al^{+3} , V^{+4} , V^{+5} , Sr^{+2} , W^{+4} , W^{+6} , Mn^{+2} , Sn^{+2} , Sn^{+4} , Pb^{+2} , Cu^{+2} , La^{+3} and Cr^{+3} . M is more preferably Zn^{+2} , Fe^{+2} , Co^{+2} , Ni^{+2} , La^{+3} and Cr^{+3} . M is most preferably Zn^{+2} .

Suitable anions A include O^{2-} , OH^- , CO_3^{2-} , HCO_3^- , PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , as well as silicate, titanate and/or zirconate ions, a halide such as chloride and bromide, nitrate, sulfate, carbonate, cyanide, oxalate, thiocyanate, isocyanate, perchlorate, isothiocyanate, an alkanesulfonate such as methanesulfonate, an arylenesulfonate such as p-toluenesulfonate, trifluoromethanesulfonate (triflate) and a C_{1-4} carboxylate.

c is preferably 5 or 6, most preferably 6; d is preferably 0 or 1, most preferably 0. b is usually 2 or 3, and is most typically 3. In most cases, c + d will equal six.

Preferred groups X include anions such as halide (especially chloride), hydroxide, sulfate, carbonate, oxalate, thiocyanate, isocyanate, isothiocyanate, C_{1-4} carboxylate and nitrite (NO_2^-), and uncharged species such as CO, H_2O and NO. Particularly preferred groups X are NO, NO_2^- and CO.

Suitable metal cyanides (apart from the selection of the complexing agent L) are described, for example, in US Patent Nos. 3,278,457, 3,278,458, 3,278,459, 3,404,109, 3,427,256, 3,427,334, 3,427,335 and 5,470,813, and copending applications 09/574,924, 09/574,923 and 09/574,925, all filed May 19, 2000, all incorporated herein by reference. All or part of L is the immiscible complexing agent.

L is miscible in a 2000 M_n poly(propylene oxide) homopolymer diol at some elevated temperature, but immiscible in that poly(propylene oxide) diol at some lower temperature at which the poly(propylene oxide) is a liquid. The elevated temperature is preferably at least 50°C , more preferably at least 80°C , even more preferably at least 100°C and especially at least 120°C . L is preferably immiscible in that poly(propylene oxide) at 25°C , more preferably at 50°C , even more preferably at 80°C and most preferably at 100°C .

Suitable complexing agents L include materials having a melting temperature between 25°C and 150°C , preferably from 40°C to 120°C , especially from about 60°C to about 110°C . An example of such a complexing agent L is a poly(ethylene oxide) having a melting temperature of from 40 - 65°C . Another

suitable complexing agent L is a block copolymer containing poly(oxyethylene) blocks and one or more blocks of another polymer, preferably having a melting temperature within the aforementioned ranges. An example of such as block copolymer is one having a poly(oxyethylene block) and a polyether block of a different monomer or monomers (such as propylene oxide, butylene oxide, tetramethylene oxide, mixtures of them or mixtures of them with ethylene oxide). Another example of such a block copolymer is one of an olefin, such as ethylene and/or propylene (preferably ethylene) with ethylene oxide. Other examples are block copolymers having a polyester (such as poly-ε-caprolactone) or poly(vinyl aromatic) (such as polystyrene) block. In the block copolymers, the oxyethylene blocks have a weight of 100 daltons or more, preferably 150-10,000 daltons, especially 150-3000 daltons. A particularly suitable complexing agent L is a block copolymer having a polyethylene or polypropylene block having a weight of 150-2000 daltons and a poly(ethylene oxide) block having a molecular weight of about 150-2000 daltons.

The metal cyanide catalyst can be made by reacting a solution of a metal cyanide compound (i.e., the acid or its corresponding alkali metal or ammonium salt) with a soluble metal salt, an insoluble metal salt or a metal. The metal cyanide catalyst precipitates. The precipitated catalyst can be isolated (by, for example, filtration) and then washed one or more times with the complexing agent L, or a solution of L in water or an organic solvent such as methanol. The catalyst then can be dried and recovered.

A preferred method of making the catalyst is to form the catalyst as a slurry in an excess of the complexing agent L, or in a mixture of the complexing agent L and a non-volatile initiator compound and/or a polyether. Methods of preparing metal cyanide catalysts directly as a slurry in an initiator compound are described in copending application 09/574,847, filed May 19, 2000, provisional application 60/365,666, filed March 19, 2002 entitled METHOD FOR PREPARING METAL CYANIDE CATALYSTS USING INSOLUBLE METAL SALTS, and provisional application 60/366,759, filed May 21, 2002 entitled Method for Preparing Metal Cyanide Catalysts Using Zero Valent Metals, both incorporated herein by reference. In these slurry processes, it is preferred to use an acidic alkali metal cyanide compound as a starting material, and react that with a metal, a soluble salt of the metal and/or an insoluble salt of the metal. The reaction is conducted in water or an organic solvent medium, or, if L is a liquid at the

temperature of the reaction, L. If the reaction is conducted in water or an organic solvent medium, the resulting slurry can be mixed with the complexing agent L (or mixture thereof) and then stripped if desired to remove water and/or one or more components of the solvent medium.

5 The catalyst complex of the invention is useful to polymerize alkylene oxides to make polyethers. In general, the process includes mixing a catalytically effective amount of the catalyst with an alkylene oxide under polymerization conditions and allowing the polymerization to proceed until the supply of alkylene oxide is essentially exhausted. The concentration of the catalyst is selected to
10 polymerize the alkylene oxide at a desired rate or within a desired period of time. An amount of catalyst sufficient to provide from about 5 to about 100,000 parts by weight metal cyanide catalyst (calculated as $M_b[M^1(CN)_r(X)_t][M^2(X)_s]_d \cdot nM^3A_y$, exclusive of any associated water and initiator) per million parts combined weight of alkylene oxide, and initiator and comonomers, if present. More preferred
15 catalyst levels are from about 20, especially from about 30, to about 50,000, more preferably to about 10,000 ppm, even more preferably to about 1500 ppm, on the same basis. Somewhat higher catalyst levels can be used, compared to most other DMC catalysts, due to the relative ease of removal of the catalysts of the invention.

 Among the alkylene oxides that can be polymerized with the catalyst
20 complex of the invention are ethylene oxide, propylene oxide, 1,2-butylen oxide, styrene oxide, epichlorohydrin and mixtures thereof. Various alkylene oxides can be polymerized sequentially to make block copolymers. More preferably, the alkylene oxide is propylene oxide or a mixture of propylene oxide and ethylene oxide and/or butylene oxide. Especially preferred are propylene oxide alone or a
25 mixture of at least 70 weight %, especially up to 85 weight %, propylene oxide and up to about 30, especially 15, weight % ethylene oxide.

 In addition, monomers that will copolymerize with the alkylene oxide in the presence of the catalyst complex can be used to prepare modified polyether polyols. Such comonomers include oxetanes as described in U.S. Patent Nos. 3,278,457 and
30 3,404,109, and anhydrides as described in U.S. Patent Nos. 5,145,883 and 3,538,043, which yield polyethers and polyester or polyetherester polyols, respectively. Hydroxyalkanoates such as lactic acid, 3-hydroxybutyrate, 3-hydroxyvalerate (and their dimers), lactones and carbon dioxide are examples of other suitable monomers that can be polymerized with the catalyst of the
35 invention.

The product polymer is preferably one in which the complexing agent L exhibits temperature-dependent miscibility, i.e. it is miscible in the product at a higher temperature but immiscible in the product at some lower temperature at which the product is a liquid. Most preferred product polymers are homopolymers of propylene oxide, random copolymers of propylene oxide and a small quantity (up to 30% by weight, especially up to about 15% by weight) of ethylene oxide, or a block copolymer of propylene oxide (or random copolymer as above) and ethylene oxide or other material.

The polymerization reaction typically proceeds well at temperatures from about 25 to about 150°C or more, preferably from about 80-130°C. A convenient polymerization technique involves charging the catalyst to a reactor and pressurizing the reactor with the alkylene oxide. An initiator compound is generally added prior to the introduction of the monomers. Polymerization proceeds after a short induction period as indicated by a loss of pressure in the reactor. Once the polymerization has begun, additional alkylene oxide is conveniently fed to the reactor on demand until enough alkylene oxide has been added to produce a polymer of the desired equivalent weight. Short induction periods are often seen.

Another convenient polymerization technique is a continuous method. In such continuous processes, the activated catalyst is continuously fed into a continuous reactor such as a continuously stirred tank reactor (CSTR) or a tubular reactor. A feed of alkylene oxide is introduced into the reactor and the product continuously removed. Initiator can be added continuously or intermittently, with the catalyst (such as in the form of a catalyst slurry in the initiator) or as a separate stream. Those catalysts exhibiting a particularly short induction period, such as less than 15 minutes, preferably less than 10 minutes, and especially less than 5 minutes, are particularly suitable for use in processes where the catalyst is added continuously.

The catalyst of this invention is especially useful in making propylene oxide homopolymers and random copolymers of propylene oxide and up to about 15 weight percent ethylene oxide (based on all monomers). The polymers of particular interest have a hydroxyl equivalent weight of from about 800, preferably from about 1000, to about 5000, preferably about 4000, more preferably to about 2500, and unsaturation of no more than 0.025 meq/g, preferably from about 0.005 to 0.02 meq/g.

During the polymerization reaction, the temperature is preferably high enough that the catalyst disperses in the forming polymer. This allows for excellent reaction efficiencies. In the preferred case where the catalyst has temperature-dependent miscibility in the polymer, the immiscible complexing agent becomes immiscible as the polymer is removed from the reaction vessel and cooled, and will phase separate or precipitate from the product. The metal catalyst separates with the complexing agent. Thus, by decanting or filtering (or other method of physical separation), the metal cyanide catalyst is quickly and easily removed from the product.

The product polymer may have various uses, depending on its molecular weight, equivalent weight, functionality and the presence of any functional groups. Polyether polyols so made are useful as raw materials for making polyurethanes. Polyethers can also be used as surfactants, hydraulic fluids, as raw materials for making surfactants and as starting materials for making aminated polyethers, among other uses.

The following examples are provided to illustrate the invention, but are not intended to limit its scope. All parts and percentages are by weight unless otherwise indicated. Catalyst loadings are calculated from the starting materials and ignoring any associated water and initiator.

Example 1

$\text{K}_3\text{Co}(\text{CN})_6$ (FW 332.35, 20.0 g, 60.18 mmol) is dissolved in deionized water (51.6 g). A solution of 96% H_2SO_4 (18.44 g, approximately 180.5 mmol H_2SO_4) is added slowly dropwise over about 10 minutes to the stirred solution of $\text{K}_3\text{Co}(\text{CN})_6$. A light yellow solution is obtained, which is cooled to 40°C with stirring. Methanol (80 g) is added to the solution over 10 minutes. During the addition, K_2SO_4 and/or KHSO_4 precipitates as a granular white solid. The resultant slurry is stirred for 5-10 minutes while cooling to 35°C. The slurry is placed in an ice water bath, stirred for 30 minutes, and vacuum filtered to remove the precipitate. The salt cake is rinsed with methanol (18 g total) to aid in deliquoring; the rinses are combined with the filtrate. The filtrate is a light yellow, clear solution weighing 177.47 g, containing a maximum of 7.39% $\text{H}_3\text{Co}(\text{CN})_6$.

8.85 g of the $\text{H}_3\text{Co}(\text{CN})_6$ solution (which contains about 2.7-3.0 mmol $\text{H}_3\text{Co}(\text{CN})_6$), are added dropwise over 30 minutes with stirring to a slurry of ZnO (0.73 g, 9.0 mmol), ZnCl_2 (0.20 g, 1.5 mmol) and polyethylene-block-poly(ethylene

glycol) copolymer (M_n total 875, PE block 700, PEG block 175, 5.18 g) in methanol (100 g). A small quantity of methanol is used to rinse the equipment. Most of the ZnO disappears as it reacts during the addition. The slurry is stirred for 10 minutes after the addition is completed. Finely divided particles of DMC catalyst are suspended in a liquid phase. Some unreacted ZnO remains.

Another 45 g of the polyethylene-block-poly(ethylene glycol) copolymer is then added. Additional methanol (80 g) is added to improve mixing. The slurry is heated at atmospheric pressure to 80°C, forming a thick, waxy material. Additional methanol is added to thin the mixture. The mixture is then heated at 80°C under slight vacuum to remove part of the methanol. A viscous, semi-solid material is obtained. This is dried under 15-30 Torr (2-4 kPa) at 70°C to form a flaky solid. The material is heated further, to 110-120°C under 15-30 Torr (2-4 kPa) vacuum, at which temperature it melts and devolatilizes. The product is cooled and forms a hard waxy solid. The final product weighs 50.54 g and contains about 3.07% dispersed DMC catalyst particles.

Example 2

$K_3Co(CN)_6$ (FW 332.35, 20.0 g, 60.18 mmol) is dissolved in deionized water (35 g). A solution of 96% H_2SO_4 (17.82 g, approximately 180 mmol H_2SO_4) is added slowly dropwise over about 15 minutes to the stirred solution of $K_3Co(CN)_6$. A light yellow solution is obtained, which is cooled to 40°C with stirring. Methanol is added to the solution over 10 minutes. During the addition, K_2SO_4 and/or $KHSO_4$ precipitates as a granular white solid. The resultant slurry is stirred for 5-10 minutes while cooling to 35°C. The slurry is placed in an ice water bath, stirred for 30 minutes, and vacuum filtered to remove the precipitate. The salt cake is rinsed with methanol (18 g total) to aid in deliquoring; the rinses are combined with the filtrate. The filtrate is a light yellow, clear solution weighing 494 g, containing a maximum of 2.66% $H_3Co(CN)_6$.

24.59 g of the $H_3Co(CN)_6$ solution (which contains about 2.7-3.0 mmol $H_3Co(CN)_6$), are added dropwise over 35 minutes with stirring to a solution of $ZnCl_2$ (1.23 g, 9 mmol) and polyethylene oxide (diol, 3350 M_w , 1.60 g) in methanol (15 g). A small quantity of methanol is used to rinse the equipment. The slurry is stirred for 25 minutes after the addition is completed. Finely divided particles of DMC catalyst are suspended in a liquid phase.

The slurry is heated under vacuum at temperatures increasing to 80°C and

vacuum increasing to 15-30 Torr (2-4 pKa). The resulting solid is dried overnight at 50°C/15-30 Torr (2-4 kPa) to produce a clear, waxy solid. This solid is then further dried for about 5 hours at 90°C/15-30 Torr (2-4 pKa). The final product weighs 3.58 g and contains about 43.4% dispersed DMC catalyst particles.

5

Example 3

24.59 g of the $\text{H}_3\text{Co}(\text{CN})_6$ solution from example 2 (which contains about 2.7-3.0 mmol $\text{H}_3\text{Co}(\text{CN})_6$), are added dropwise over 35 minutes with stirring to a solution of ZnCl_2 (1.23 g, 9 mmol) and polyethylene oxide (diol, 3350 M_w , 5.0 g) in methanol (20.6 g). A small quantity of methanol is used to rinse the equipment. The mixture is heated slightly to dissolve the polyethylene oxide. The slurry is stirred for 10 minutes after the addition is completed. Finely divided particles of DMC catalyst are suspended in a liquid phase. An additional 71.6 grams of the polyethylene oxide are then stirred in.

15 The slurry is heated under vacuum at temperatures increasing to 80°C and vacuum increasing to 15-30 Torr (2-4 pKa). The resulting solid (which melts at 75-80°C) weighs about 77.6 g and contains about 2.0% dispersed DMC catalyst particles.

20 Example 4

$\text{K}_3\text{Co}(\text{CN})_6$ (FW 332.35, 20.0 g, 60.18 mmol) is dissolved in deionized water (46.6 g) and heated to 45°C. A solution of 96% H_2SO_4 (18.44 g, approximately 180.5 mmol H_2SO_4) is added slowly dropwise over about 10 minutes to the stirred solution of $\text{K}_3\text{Co}(\text{CN})_6$. A light yellow solution is obtained, which is cooled to about 25 45°C with stirring. Methanol (200 g) is added to the solution over 5 minutes. During the addition, K_2SO_4 and/or KHSO_4 precipitates as a granular white solid. The resultant slurry is stirred for 50 minutes while cooling toward room temperature. The slurry is placed in an ice water bath, stirred for 30 minutes, and vacuum filtered at 15°C to remove the precipitate. The salt cake is rinsed with 30 methanol (18 g total) to aid in deliquoring; the rinses are combined with the filtrate. The filtrate is a light yellow, clear solution weighing 290.5 g, containing a maximum of 4.52 wt.-% $\text{H}_3\text{Co}(\text{CN})_6$.

143.63 g of the $\text{H}_3\text{Co}(\text{CN})_6$ solution (which contains about 29.75 mmol $\text{H}_3\text{Co}(\text{CN})_6$), are added dropwise over 125 minutes with stirring to a slurry of ZnO (8.73 g, 107.2 mmol) in methanol. A small quantity of methanol is used to rinse the 35

equipment. Most of the ZnO disappears as it reacts during the addition. The slurry is stirred for about a day after the addition is completed. Some unreacted ZnO remains. About 145.49 grams of DMC slurry are obtained.

5 A slurry of polyethylene-block-poly(ethylene glycol) copolymer (M_n total 1400, PE block 700, PEG block 700, 90.40 g) in toluene (904 g) is heated to 80°C with stirring at atmospheric pressure in a 2 stripping flask to dissolve the copolymer. The solution is then cooled to 60°C. The DMC slurry is added in several small portions. After each portion of DMC slurry is added, the methanol is distilled at 60°C/up to about 125 Torr (~17kPa) vacuum and slight nitrogen sweep.
10 Some water/toluene azeotrope and possibly some toluene is also removed during these distillation steps. Following the final addition of DMC slurry, the bulk of methanol is removed at 60°C/~125 Torr (~17 kPa) vacuum, and then the temperature and vacuum are gradually increased to 80°C and 15-30 Torr (2-4 kPa) for 160 minutes. At this point, 106.97 grams of DMC/copolymer slurry in mainly
15 toluene remain. 104.19 g of this are transferred into a glass bottle and heated at 120°C/~125 Torr (~17 pKa) vacuum with slight nitrogen sweep for 5-6 hours. The temperature and vacuum are then increased to 150°C/15-30 Torr (2-4 kPa) (no nitrogen sweep) for 2 hours. An opaque, waxy solid is obtained when the product is cooled to room temperature, having a mass of 95.12 g and containing about 4.87
20 wt.-% of the DMC catalyst.

A glass vial is charged with 0.0037 g of the solid catalyst slurry, 0.1239 g of Voranol 2070™ polyol (a 700 molecular weight poly(propylene oxide triol), and 0.5823 g of propylene oxide, sealed and heated to 90°C for 21 hours. The progress of the reaction is followed visually. 100% of the propylene oxide is converted to
25 polymer after 21 hours of polymerization. The final reaction product is visually clear at 110°C, indicating that at that temperature the catalyst complex is miscible in the product poly(propylene oxide). However, upon cooling to 90°C, the product becomes opaque as the catalyst complex phase separates. The phase-separated catalyst is then removable by filtration and/or centrifugation techniques.

WHAT IS CLAIMED IS:

1. A metal cyanide catalyst complexed with a complexing agent that is
5 miscible in a 2000 M_n poly(propylene oxide)homopolymer diol at an elevated temperature, but which is not miscible in the poly(propylene oxide) at a lower temperature at which the poly(propylene oxide) is a liquid.
2. The metal cyanide catalyst of claim 1, wherein the elevated temperature is at least 50°C and the lower temperature is at least 25°C.
- 10 3. The metal cyanide catalyst of claim 2, wherein the elevated temperature is at least 80°C and the lower temperature is at least 25°C.
4. The metal cyanide catalyst of claim 3, wherein the elevated temperature is at least 100°C and the lower temperature is at least 25°C.
5. The metal cyanide catalyst of claim 4, wherein the elevated temperature is
15 at least 130°C and the lower temperature is at least 25°C.
6. The metal cyanide catalyst of claim 1, wherein the complexing agent is a poly(ethylene oxide) polymer or a block copolymer having a poly(ethylene oxide) block and a block of another monomer or monomers.
7. The metal cyanide catalyst of claim 6, wherein the complexing agent is a
20 block copolymer having a poly(ethylene oxide) block and a block of polyethylene or polypropylene.
8. The metal cyanide catalyst of claim 7, wherein the poly(ethylene oxide) block has a weight of 150-2000 daltons and the polyethylene or polypropylene block has a weight of 150-2000 daltons.
- 25 9. The metal cyanide catalyst of claim 1 wherein the metal cyanide is a zinc hexacyanocobaltate.
10. A metal cyanide catalyst complexed with an immiscible complexing agent comprising poly(ethylene oxide) polymer or block copolymer having poly(ethylene oxide) blocks and blocks of another monomer or monomers, wherein the immiscible
30 complexing agent has a melting temperature between 25°C and 150°C.
11. A process wherein a metal cyanide catalyst is mixed with an alkylene oxide and the resulting mixture subjected to conditions including an elevated temperature sufficient to polymerize the alkylene oxide to form a poly(alkylene oxide), wherein the metal cyanide catalyst is complexed with a complexing agent
35 which is miscible in the poly(alkylene oxide) at the elevated temperature, but

which is not miscible in the poly(alkylene oxide) at a lower temperature at which the poly(alkylene oxide) is a liquid .

12. The process of claim 11 wherein the alkylene oxide comprises propylene oxide.

5 13. The process of claim 12 wherein the poly(alkylene oxide) is subsequently cooled to a temperature at which the poly(alkylene oxide) is a liquid and at which the complexing agent is not miscible in the poly(alkylene oxide).

14. The process of claim 13 wherein the metal cyanide catalyst is removed from the cooled poly(alkylene oxide).

10 15. The process of claim 14 wherein the metal cyanide catalyst is removed from the cooled poly(alkylene oxide) by filtration.

16. The process of claim 11, wherein the complexing agent is a poly(ethylene oxide) polymer or a block copolymer having a poly(ethylene oxide) block and a block of another monomer or monomers.

15 17. The process of claim 16, wherein the complexing agent is a block copolymer having a poly(ethylene oxide) block and a block of polyethylene or polypropylene.

18. The process of claim 17, wherein the poly(ethylene oxide) block has a weight of 150-2000 daltons and the polyethylene or polypropylene block has a weight of 150-2000 daltons.

20 19. A process wherein a metal cyanide catalyst is mixed with an alkylene oxide and the resulting mixture subjected to conditions including an elevated temperature sufficient to polymerize the alkylene oxide to form a poly(alkylene oxide), wherein the metal cyanide catalyst with an immiscible complexing agent comprising a poly(ethylene oxide) polymer or block copolymer having poly(ethylene
25 oxide) blocks and blocks of another monomer or monomers, wherein the immiscible complexing agent has a melting temperature between 25°C and 150°C.

20. A polymer made in the process of claim 11.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J27/26 05/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 291 388 B1 (HOFMANN JOERG ET AL) 18 September 2001 (2001-09-18) column 3, line 40 -column 5, line 29 examples	1-20
X	DE 199 57 105 A (BASF AG) 31 May 2001 (2001-05-31) column 2, line 50 -column 3, line 41 examples 2,3	1-20
X	WO 01 04184 A (DOW CHEMICAL CO) 18 January 2001 (2001-01-18) page 7, line 27 -page 9, line 12 example 1	1-20
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

30 June 2003

Date of mailing of the international search report

04/07/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Besselmann, S

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 19063 A (KUMPF ROBERT JOSEPH ;SCHNEIDER MICHAEL (DE); HOFMANN JOERG (DE); 0) 22 April 1999 (1999-04-22) examples 3,7 ---	1-20
X A	EP 0 776 922 A (ARCO CHEM TECH) 4 June 1997 (1997-06-04) examples ---	20
X A	EP 0 743 093 A (ARCO CHEM TECH) 20 November 1996 (1996-11-20) table 5 -----	20

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1, 11, 20 (all partially)
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1, 11, 20 (all partially)

Present claim 1 relates to a product defined by reference to a desirable characteristic or property, namely the miscibility of the complexing agent in a 2000 Mn poly(propylene oxide) homopolymer diol at an "elevated" and a "lower" temperature. The claim covers all products having this characteristic or property, whereas the application provides support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT for only a very limited number of such products. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claim also lacks clarity (Article 6 PCT).

Consequently, the search of claim 1 has been carried out for those parts of the claim which appear to be clear, namely those parts relating to the compounds defined in claim 6. The search of the dependent claims has been restricted accordingly.

The same considerations apply to claim 11 relating to a process. Consequently, the search of claim 11 has been carried out for those parts relating to the processes defined in claim 16. The search of the dependent claims and of claim 20 has been restricted accordingly.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6291388	B1	18-09-2001	DE 19810269 A1	11-05-2000
			AT 239548 T	15-05-2003
			AU 2929199 A	27-09-1999
			AU 9542598 A	03-05-1999
			BR 9813034 A	15-08-2000
			BR 9908594 A	14-11-2000
			CA 2306378 A1	22-04-1999
			CA 2322823 A1	16-09-1999
			CN 1275929 T	06-12-2000
			CN 1292727 T	25-04-2001
			DE 59905468 D1	12-06-2003
			WO 9919063 A1	22-04-1999
			WO 9946042 A1	16-09-1999
			EP 1034035 A1	13-09-2000
			EP 1071509 A1	31-01-2001
			HU 0105448 A2	29-04-2002
			JP 2001519468 T	23-10-2001
			JP 2002506088 T	26-02-2002
			US 6323375 B1	27-11-2001
DE 19957105	A	31-05-2001	DE 19957105 A1	31-05-2001
			AU 1701201 A	04-06-2001
			WO 0138421 A1	31-05-2001
			EP 1237985 A1	11-09-2002
WO 0104184	A	18-01-2001	AU 5920800 A	30-01-2001
			BR 0011793 A	12-03-2002
			CA 2376201 A1	18-01-2001
			CN 1358209 T	10-07-2002
			EP 1204695 A1	15-05-2002
			JP 2003504469 T	04-02-2003
			WO 0104184 A1	18-01-2001
			US 6552163 B1	22-04-2003
WO 9919063	A	22-04-1999	DE 19745120 A1	15-04-1999
			DE 19757574 A1	24-06-1999
			DE 19810269 A1	11-05-2000
			DE 19834573 A1	03-02-2000
			DE 19842382 A1	23-03-2000
			AU 1148599 A	03-05-1999
			AU 9542598 A	03-05-1999
			BR 9813034 A	15-08-2000
			BR 9813040 A	15-08-2000
			CA 2306378 A1	22-04-1999
			CA 2306386 A1	22-04-1999
			CN 1275096 T	29-11-2000
			CN 1275929 T	06-12-2000
			WO 9919062 A1	22-04-1999
			WO 9919063 A1	22-04-1999
			EP 1034035 A1	13-09-2000
			EP 1034036 A1	13-09-2000
			JP 2001519467 T	23-10-2001
			JP 2001519468 T	23-10-2001
			US 2002068812 A1	06-06-2002
			US 6323375 B1	27-11-2001
			AU 2270599 A	19-07-1999
			BR 9814402 A	10-10-2000
			CA 2315766 A1	08-07-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date				
WO 9919063	A	CN	1107542 B	07-05-2003			
		WO	9933562 A1	08-07-1999			
		EP	1051253 A1	15-11-2000			
		HU	0004519 A2	28-04-2001			
		JP	2001527132 T	25-12-2001			
		AT	239548 T	15-05-2003			
		AU	2929199 A	27-09-1999			
		BR	9908594 A	14-11-2000			
		CA	2322823 A1	16-09-1999			
		CN	1292727 T	25-04-2001			
		DE	59905468 D1	12-06-2003			
		WO	9946042 A1	16-09-1999			
		EP	1071509 A1	31-01-2001			
		HU	0105448 A2	29-04-2002			
		JP	2002506088 T	26-02-2002			
		US	6291388 B1	18-09-2001			
		AU	5411899 A	28-02-2000			
		BR	9912604 A	02-05-2001			
		CA	2338657 A1	17-02-2000			
		CN	1311716 T	05-09-2001			
		WO	0007721 A1	17-02-2000			
		EP	1115488 A1	18-07-2001			
		HU	0102708 A2	28-11-2001			
		JP	2002522567 T	23-07-2002			
		AU	5859299 A	03-04-2000			
		BR	9913841 A	12-06-2001			
		EP 0776922	A	04-06-1997	US	5688861 A	18-11-1997
					AT	214404 T	15-03-2002
					AU	722568 B2	03-08-2000
					AU	7404396 A	05-06-1997
					BR	9605748 A	25-08-1998
					CA	2188965 A1	31-05-1997
CN	1396190 A				12-02-2003		
CN	1156731 A , B				13-08-1997		
DE	69619770 D1				18-04-2002		
DE	69619770 T2				24-10-2002		
DK	776922 T3				03-06-2002		
EP	0776922 A1				04-06-1997		
ES	2173258 T3				16-10-2002		
JP	9157385 A				17-06-1997		
SG	81905 A1				24-07-2001		
TW	430676 B				21-04-2001		
US	6143802 A				07-11-2000		
US	5955534 A				21-09-1999		
ZA	9609938 A				23-06-1997		
EP 0743093	A	20-11-1996	US	5712216 A	27-01-1998		
			AT	210500 T	15-12-2001		
			AU	703219 B2	18-03-1999		
			AU	5228196 A	01-08-1996		
			BR	9602262 A	23-06-1998		
			CA	2175266 A1	16-11-1996		
			CN	1140181 A , B	15-01-1997		
			DE	69617795 D1	24-01-2002		
			DE	69617795 T2	19-09-2002		
			DK	743093 T3	08-04-2002		
			EP	0743093 A1	20-11-1996		

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0743093	A	ES 2169210 T3	01-07-2002
		HU 9601280 A2	28-03-1997
		JP 3376212 B2	10-02-2003
		JP 8311171 A	26-11-1996
		SG 55200 A1	21-12-1998
		TW 470756 B	01-01-2002
		TW 460494 B	21-10-2001
		US 6018017 A	25-01-2000
		ZA 9603581 A	07-11-1997
